

AIRBORNE MEASUREMENTS OF GASES AND PARTICLES FROM AN ALASKAN WILDFIRE

J. David Nance, Peter V. Hobbs, and Lawrence F. Radke¹

Cloud and Aerosol Research Group, Department of Atmospheric Sciences,
University of Washington, Seattle

Darold E. Ward

Intermountain Fire Science Laboratory, USDA Forest Service, Missoula, Montana

Abstract. Airborne measurements of several gaseous and particulate chemical species were obtained in the emissions from a wildfire that burned in an old black spruce forest in Alaska during the summer of 1990. The relative proportions of most of the measured plume constituents are consistent with ground-based and airborne measurements in the plumes of several other biomass fires, and with laboratory measurements. Possible exceptions include the mean fine-particle emission factor, which was about 3 times larger than predicted from a regression relation based on measurements of the smoke from several prescribed biomass fires, and the mean CH₄/CO molar emission ratio which was at the low end of a range of values measured for other biomass fires. Measurements of water-soluble particulate ions in the smoke plume from the Alaskan wildfire indicate that acids formed from the oxides of sulphur and nitrogen were partially neutralized inside cloud droplets by NH₃ absorbed from the plume.

Introduction

Wildfires in the State of Alaska, in the Yukon and Northwest Territories of Canada, and in Siberia, contribute substantial quantities of trace gases and aerosols to the atmosphere. Such fires are often a major feature of the arctic region during summer. For example, in Alaska, wildfires sometimes occur over an area of 1 million ha (10⁴ km²) in a year, yet measurements of the emissions from biomass fires burning in this important region have not been previously reported.

On June 27–28, 1990, members of the Cloud and Aerosol Research (CAR) Group of the University of Washington (UW) carried out three research flights for the purpose of characterizing the smoke emissions from a wildfire located in the Yukon Flats area of Alaska at 66° 37' N latitude and 147° 50' W longitude. This fire was designated A121 by the Alaska Fire Service, and we will also refer to it by this number. Wildfire A121 marked the beginning of a severe fire episode in Alaska, which extended for 8 weeks ending in late August 1990.

Fire A121 started on June 26, following a period of lightning in the Yukon River area, about 160 km due north of Fairbanks. The first UW flight was made on June 27 between 1700 and 2000 PDT. The fire, which was about 200 ha in size at this time, was burning in an old black spruce

forest on a reasonably level alluvial plane about 20 km north of the Yukon River. At the time of our arrival, the wind was from the southwest, and the upwind side of the fire was nearly extinguished. Advancement of the fire on the downwind side was impeded by a small lake and by a large discontinuity in the fuel supply. The fire was spreading only modestly along its flanks through ground litter fuels, with occasional torching of single trees. Fire suppression efforts included a retardant drop and a crew of smoke jumpers that parachuted to the fire on the morning of June 27, and began work on a fireline along the south flank of the fire. Between 2000 and 2200 PDT on June 27, immediately following the departure of the UW aircraft from the vicinity of the fire, the wind shifted to the northwest, and A121 jumped a partially completed control line and began spreading toward the southeast, increasing in size from ~200 ha to over 2000 ha. From this time onward, A121 was a free-burning wildfire limited only by prevailing weather and fuel conditions.

On June 28, 1990, the CAR Group made two flights, the first from 1400 to 1730 PDT and the second from 1915 to 2300 PDT. A121 burned toward the northeast and doubled in size on June 28, but at no time did it sustain a crown fire. The primary activity was a low-intensity ground fire that burned through the top layer of needles on the ground. There was an occasional torching of tree crowns, however the litter and duff fuels that lay beneath the surface layer of needles were not dry enough to sustain combustion. Consequently, the fire advanced along distinct narrow fronts with little smoldering in the wakes of the fronts. This led to the rapid dilution of the smoke plume by efficient mixing with ambient air.

In this paper, we present airborne measurements of several gaseous and particulate trace species measured in the smoke plume from A121. Parameters that describe the relative proportions of various emissions released are computed and used for comparison with other biomass fires. These measurements are of particular interest because there are very few estimates of emissions from wildfires and even fewer from fires in boreal forests.

Measurements and Methods

Sampling was carried out aboard the CAR Group's Convair C-131 research aircraft. A wide range of instruments, and a combination of continuous and "grab" sampling techniques, provided measurements of a number of gaseous and particulate trace species. The instrumentation aboard the aircraft and calibration procedures have been described by Hobbs et al. [1991]. The measuring techniques and methods of analysis used in this study are described briefly below.

During passes through the smoke plume, "grab" samples of air were collected in a 1.5 m³ polyethylene bag that was

¹ Now at National Center for Atmospheric Research, Boulder, Colorado.

TABLE 1. Mixing Ratio of Gases and Mass Concentrations of Particles Measured in and Around the Smoke Plume From the Alaskan Wildfire

Date, 1990	Time, PDT	Sample Type*	CO ₂ , [†] ppm	CO, ppb	CH ₄ , ppb	C ₂ H ₆ , ppb	C ₂ H ₂ , ppb	C ₃ H ₈ , ppb	C ₃ H ₆ , ppb	NMHC, [‡] ppbC	N ₂ O, ppb	NH ₃ , ppb	NO _x , [†] ppb	NH ₄ ⁺ , µg m ⁻³	NO ₃ ⁻ , µg m ⁻³	SO ₄ ⁻ , µg m ⁻³	PM _{3.5} , [#] µg m ⁻³
June 27	1815	Fresh smoke	17.3	1689	1924	23.1	4.8	7.1	8.7	247.8	341.4	NM	18.1	NM	NM	NM	261
	1856	Fresh smoke	14.3	1284	1823	14.4	6.4	3.5	7.7	214.9	340.0	NM	14.5	NM	NM	NM	487
June 28	1456	Smoke sampled after passage through cloud	NM	NM	NM	NM	NM	NM	NM	NM	NM	0.4	NM	0.72	0.82	0.73	122
	1513	Fresh smoke	23.6	1294	1879	8.2	4.7	1.9	5.0	134.3	340.9	10.6	20.4	0.40	0.85	0.94	528
	1531	Fresh smoke	14.7	1309	1841	8.6	3.9	1.9	4.5	125.9	342.2	13.6	15.1	0.54	1.41	0.63	414
	1551	Background	NA	91	1806	2.0	0.2	0.9	0.1	35.8	340.4	0.4	NA	BDL	BDL	0.09	36
	1648	Fresh smoke	28.1	2304	1950	13.2	6.7	4.0	8.2	223.3	341.9	NM	25.6	NM	NM	NM	751
	2041	Aged smoke	18.7	1550	1886	10.4	4.9	2.4	5.2	139.2	340.5	26.9	12.6	0.35	3.44	1.16	550
	2119	Fresh smoke	17.6	1402	1880	8.6	4.5	1.9	4.1	108.7	341.5	22.3	13.2	4.37	3.43	1.28	548
	2135	Background	NA	106	1792	1.0	0.1	0.2	0.1	29.9	339.0	5.3	NA	0.38	BDL	0.08	NA
	2148	Fresh smoke	18.9	1742	1899	11.1	5.2	2.6	5.9	150.9	342.0	33.2	18.7	2.46	2.07	0.90	475
	2206	Old smoke	20.0	NM	NM	NM	NM	NM	NM	NM	NM	11.5	NM	1.04	4.87	1.56	523

NM denotes not measured, and BDL denotes below detectable limit.

* Smoke samples labeled "fresh" were obtained within a distance of ~5 km from the main fire. The "aged" smoke sample was obtained ~15 km downwind, and the "old" smoke sample was collected over 20 km downwind of the fire.

† Plume minus background measurements. (NO_x = NO + NO₂; on average, ~85% of NO_x is NO₂.)

‡ Nonmethane hydrocarbons (from C₂ to C₁₀, with ethene omitted).

Total mass of particles with aerodynamic diameters <3.5 µm.

filled with ram air pressure. The concentrations of all gaseous hydrocarbons, CO and N₂O were measured from portions of these samples that were siphoned into stainless-steel canisters. A total of 10 canisters were analyzed, eight of which contained in-plume samples, and two of which contained upwind (background) air samples. Analysis of the canister samples was performed at the Oregon Graduate Institute of Science and Technology, using the techniques (e.g., gas chromatography, mass spectroscopy, and electron capture) and methodologies described by Rasmussen et al. [1974] and Rasmussen and Khalil [1980, 1981].

Concentrations of CO₂ and NO_x in the grab samples were measured with monitors aboard the aircraft. Plume-minus-background concentrations CO₂ and NO_x were measured by deducting the ambient airstream (background) signal measured prior to plume entry from the grab sample (plume) signal. Flow to the instruments was electronically switched between the grab sample feed and the ambient airstream feed. Continuous ambient airstream measurements of the light scattering coefficient (σ_{sp}) at $\lambda = 540$ nm were provided by a nephelometer and aided in defining plume boundaries.

Teflon filters were exposed to portions of the grab samples of smoke to determine concentrations of particle mass. Particles >3.5 μ m in aerodynamic diameter were first removed by a cyclone that preceded the filter housing in the sample stream. SO₄²⁻, NO₃⁻, and NH₄⁺ ions were extracted from these samples in distilled water and measured in the laboratory. Gaseous NH₃ was collected with oxalic acid-impregnated cellulose afterfilters.

Analysis and Results

Trace gas mixing ratios (i.e., mole of a species per mole of air) and particulate mass concentrations are listed in

Table 1. Smoke samples not modified by interaction with a water cloud that briefly formed over the fire are categorized by their relative ages. Measurements performed on two grab samples of background air collected on June 28, were averaged to arrive at a "mean" background concentration; this was subsequently used as the background reference for all grab sample measurements in the smoke plume, including those of the previous day (no background samples were collected on June 27).

To facilitate comparisons with other studies, we have provided three different normalizations of the emissions measured in the plume from A121. These include emission ratios, normalized to both CO₂ and CO (i.e., $\Delta X/\Delta\text{CO}_2$ and $\Delta X/\Delta\text{CO}$, where ΔX is the above background concentration of any compound X, and ΔCO_2 and ΔCO are the above background concentrations of CO₂ and CO, respectively), and "emission factors" (i.e., the mass of a compound emitted into the atmosphere per unit mass of fuel burned). Mean emission ratios, expressed as molar percentages, and mean emission factors, expressed in units of grams per kilogram, are presented in Table 2.

Throughout this paper, when discussing emission ratios, we will attempt to adhere as much as possible to the convention proposed by Lobert et al. [1991]: that flaming stage compounds (highly oxidized compounds, including CO₂, NO_x, N₂O, and SO₂, that are produced in greatest proportion during flaming combustion) be normalized by CO₂, and that smoldering stage compounds (reduced compounds, including CO, most hydrocarbons and ammonia, that are produced in greatest proportion during smoldering combustion) be normalized by CO. The $\Delta\text{CO}/\Delta\text{CO}_2$ ratio is highly responsive to changes in the type of combustion.

We used the carbon-balance method of Ward et al. [1982] and Radke et al. [1988] to compute emission factors. In this

TABLE 2. Mean Emission Ratios Normalized With Respect to CO₂ and CO (Mole/Mole; Expressed as Percentage) and Emission Factors (Grams of Compound per Kilogram of Fuel Burned) for Particles and Trace Gases from the Alaskan Wildfire

Species	$\Delta X/\Delta\text{CO}_2$, %	$\Delta X/\Delta\text{CO}$, %	Emission Factor, g kg ⁻¹
CO ₂		1318 ± 277	1640 ± 25
CO	7.81 ± 1.24		81 ± 12
CH ₄	0.44 ± 0.17	5.7 ± 1.9	2.6 ± 1.0
C ₂ H ₆	0.059 ± 0.032	0.73 ± 0.31	0.66 ± 0.35
C ₂ H ₂	0.027 ± 0.007	0.35 ± 0.08	0.26 ± 0.07
C ₃ H ₈	0.014 ± 0.010	0.17 ± 0.11	0.23 ± 0.17
C ₃ H ₆	0.033 ± 0.012	0.42 ± 0.11	0.51 ± 0.18
NO _x *	0.087 ± 0.016	1.2 ± 0.2	1.5 ± 0.2
N ₂ O	0.009 ± 0.005	0.11 ± 0.06	0.14 ± 0.08
NH ₃	0.095 ± 0.056	1.3 ± 0.5	0.64 ± 0.31
PM _{3.5} †			21.5 ± 4.8

* NO_x = NO + NO₂. On average ~85% of NO_x is NO₂.

† Total mass of particles with aerodynamic diameters <3.5 μ m.

TABLE 3. Average Emission Factors (and Standard Deviations) for Particles and Various Trace Gases Sampled From the Plumes of 10 Biomass Fires in North America Between December 1986 and September 1989

Fire	CO ₂	CO	CH ₄	C ₂ H ₆	C ₂ H ₂	C ₃ H ₈	C ₃ H ₆	N ₂ O	NO _x *	NH ₃	PM _{3.5} †
Lodi 1	1664 ± 44	74 ± 16	2.4 ± 0.2	0.35 ± 0.12	0.32 ± 0.05	0.21 ± 0.12	0.58 ± 0.05	0.31 ± 0.14	8.9 ± 3.5	1.70 ± 0.80	13.5 ± 4.4
Lodi 2	1650 ± 31	75 ± 14	3.6 ± 0.3	0.55 ± 0.15	0.21 ± 0.03	0.32 ± 0.12	0.46 ± 0.03	0.27 ± 0.31	3.3 ± 0.8	0.09 ± 0.04	23.0 ± 19.6
Myrtle	1626 ± 39	106 ± 20	3.0 ± 0.8	0.60 ± 0.13	0.22 ± 0.04	0.25 ± 0.05	0.70 ± 0.04		2.5 ± 0.7	2.00 ± 0.90	6.1 ± 3.1
Silver	1637 ± 103	89 ± 50	2.6 ± 1.6	0.56 ± 0.33	0.19 ± 0.09	0.42 ± 0.13	0.08 ± 0.01	0.27 ± 0.39	0.8 ± 0.7	0.60 ± 0.50	20.2 ± 12.7
Hardiman	1664 ± 62	82 ± 36	1.9 ± 0.5	0.45 ± 0.26	0.31 ± 0.35	0.18 ± 0.13	0.58 ± 0.09	0.41 ± 0.52	3.3 ± 2.3	0.10 ± 0.07	10.5 ± 3.0
Eagle	1748 ± 11	34 ± 6	0.9 ± 0.2	0.18 ± 0.05	0.08 ± 0.02	0.05 ± 0.02	0.25 ± 0.06	0.16 ± 0.13	7.2 ± 3.8		11.3 ± 4.8
Battersby	1508 ± 161	175 ± 91	5.6 ± 1.7	0.57 ± 0.45	0.33 ± 0.06	0.27 ± 0.12	0.90 ± 0.15		1.1 ± 1.3		20.9 ± 10.6
Hill	1646 ± 50	90 ± 21	4.2 ± 1.3	0.48 ± 0.17	0.25 ± 0.05	0.15 ± 0.06	0.65 ± 0.19	0.18 ± 0.06			10.2 ± 6.5
Wicksstead	1700 ± 82	55 ± 41	3.8 ± 2.8	0.51 ± 0.34	0.22 ± 0.12	0.17 ± 0.12	0.62 ± 0.40	0.22 ± 0.14			10.8 ± 4.7
Mabel Lake	1660 ± 29	83 ± 37	3.5 ± 1.9	0.38 ± 0.21	0.22 ± 0.06	0.11 ± 0.07	0.46 ± 0.21	0.04 ± 0.05			12.8 ± 4.3
Overall Average	1650 ± 29	83 ± 16	3.2 ± 0.5	0.46 ± 0.08	0.24 ± 0.04	0.21 ± 0.05	0.53 ± 0.08	0.23 ± 0.05	3.9 ± 1.6	0.90 ± 0.43	14.4 ± 10.1

All values shown are based on the analyses of gases collected in stainless steel canisters and particles collected on Teflon filters.

Units are in grams per kilogram. [From Radke et al., 1991]

* NO_x = NO + NO₂. On average ~70% of NO_x is NO₂.

† Total mass of particles with aerodynamic diameters <3.5 μm.

method, it is assumed that the measurements of carbonaceous plume constituents account for all of the carbon burned. We estimate that this will artificially inflate the emission factor estimates by about 5–10% due to the neglect of ground ash and high-molecular weight, gaseous hydrocarbons in the carbon balance. In a series of laboratory fires (several fuel types), Lobert et al. [1991] found that, on average, ash accounted for 5% of the total burned fuel carbon and another 5% was unaccounted for. This was attributed to particles, which we assumed to be 60% carbon by mass based on the results of Dasch [1982], Patterson and McMahon [1984], and Ward and Hardy [1988], and gaseous hydrocarbons $> C_{10}$, which were not measured. We also assumed that the carbon content of the fuel was 50% by mass, corresponding to the chemical stoichiometry of $C_6H_9O_4$ [Bryam, 1959]. On the basis of other measurements of the carbon content of various biomass fuels [e.g., Bollen, 1974; Lobert et al., 1991; Susott et al., 1991], it is unlikely that the true mean carbon fraction of the burned Alaskan biomass differed from 50% by more than $\pm 10\%$.

In some cases, trace gas concentrations within the smoke plume were enhanced by only a few percent over background levels. For example, measured plume concentrations of CO_2 never exceeded measured background concentrations by more than 10%. It is encouraging, however, that there was little variation in the eight emission factors computed for CO_2 . In seven of the eight plume samples, the combustion efficiency (CE), defined as the percentage of carbon released from the fuel that is completely oxidized to CO_2 by the combustion process [Ward and Hardy, 1991], varied within a narrow interval between 87.9 and 89.7%. The eighth sample yielded a CE value of 92.4%. In controlled burns of logging slash that are constrained to a specific area of fuel supply, the trend from flaming to smoldering combustion produces CE values that can vary by 10% or more [Ward and Hardy, 1991]. However, A121 was a free-burning wildfire that continually advanced into fresh supplies of fuel that were incapable of supporting sustained, smoldering combustion. Thus a smaller degree of variability, with a largely random component (associated with measurement uncertainty), may be anticipated in the CO_2 normalized emissions for A121. Consequently, the averages shown in Table 2 are probably reasonably representative of the true mean emissions characteristics of A121 during the period of our measurements.

Discussion

Gases

Since 1986 we have used a research aircraft to study the emissions from a number of prescribed fires and wildfires. The averaged emission factors for several compounds from 10 of these fires are shown in Table 3. Considerable variation is evident, both between fires and within fires. This variance may result from differences in fuel characteristics (e.g., type, moisture content, spatial arrangement), changes or differences in the predominant combustion type (flaming or smoldering) and prevailing weather conditions, and propagational differences (upslope or downslope, heading or backing). In spite of these numerous potential sources of deviation, the averaged emission factors for CO_2 , CO, CH_4 , and several C_2 – C_4 hydrocarbons from A121 (Table 2) differ from their corresponding overall averages in Table 3 by a maximum of 25%. Thus, with respect to our previously collected data, regardless of fuel and combustion

characteristics, the averaged emission factors for CO_2 , CO, CH_4 , and C_2 – C_4 hydrocarbons from A121 appear fairly typical.

The mean CE computed from eight samples collected in the smoke from A121 was $89.5 \pm 1.3\%$. Ward and Hardy [1991] reported on an extensive collection of ground-based, field measurements made in the smoke from several prescribed fires with differing fuel characteristics in Washington, Oregon, and California. They derived the following empirical relations between CE and the emission factors ($g\ kg^{-1}$) for CO [EF(CO)] and CH_4 [EF(CH_4)]:

$$EF(CO) = 961 - 984\ CE \quad (r = -0.9) \quad (1)$$

$$EF(CH_4) = 42.7 - 43.2\ CE \quad (r = -0.88) \quad (2)$$

In (1) and (2), $0 \leq CE \leq 1$, and r is the correlation coefficient. The emission factor for CO_2 [EF(CO_2)] is related to CE by a simple constant derived from an assumed biomass fuel composition of 50% carbon by mass:

$$EF(CO_2) = 1833\ CE \quad (3)$$

Substituting 0.895 for CE in (1) and (2) gives emission factors of 80 and $4.0\ g\ kg^{-1}$ for CO and CH_4 , respectively. Compared with the means presented in Table 2 for A121 (81 ± 12 and $2.6 \pm 1.0\ g\ kg^{-1}$ for CO and CH_4 , respectively), there is close agreement between the CO emission factors, but the emission factor for CH_4 from A121 is only 65% of that predicted by (2). Thus the mean CH_4/CO emission ratio of $5.7 \pm 1.9\%$ for A121 is similarly diminished with respect to the 8.8% figure derived from (1) and (2).

The averaged $\Delta X/\Delta CO_2$ and $\Delta X/\Delta CO$ emission ratios for many gaseous carbon compounds emitted from A121 are very close to values reported by Lobert et al. [1991] for a series of laboratory measurements on several different types of biomass fuel (Table 4).

The agreement between the two mean CO/CO_2 emission ratios (7.3%, from Lobert et al. [1991] and 7.8% from A121) can be considered largely coincidental in view of the strong dependence of this parameter on the type of combustion. Lobert et al. [1991] report a range of values from 3 to 16%. Similarly, for the 10 fires listed in Table 3, the average CO/CO_2 emission ratio ranges from 3% (Eagle prescribed burn) to 18% (Battersby prescribed burn) with an overall average of 8%. (The two wildfires in Table 3, Myrtle/Fall Creek and Silver, have means of 10% and 8.5%, respectively.) Greenberg et al. [1984] report CO/CO_2 emission ratios ranging from 5 to 30%, with a mean of 11.5%, from their ground-based, field measurements in Brazil. Andreae et al. [1988] report a range of 6–16%, with a mean of 8.5%, from their airborne measurements in Brazil. Cofer et al. [1991] report a range of 5–12%, averaged according to ecosystem and burning stage, from their low-altitude, helicopter measurements in North America.

Our measurements of the mean $\Delta X/\Delta CO$ emission ratios for ethane (C_2H_6), propane (C_3H_8) and propene (C_3H_6) from A121 agree with the values reported by Lobert et al. [1991] to within 15%, although the variances in both sets of measurements are generally high. Similar ratios can be derived from the results of Greenberg et al. [1984] if their mean $\Delta X/\Delta CO_2$ ratios for hydrocarbons are divided by their mean CO/CO_2 ratio (Table 4). The mean emission ratios for methane (CH_4/CO) and acetylene (C_2H_2/CO_2) from A121 were about 35–40% less than those reported by Lobert et al. [1991].

Since CH_4 and CO are both smoldering stage compounds, the CH_4/CO emission ratio should be less dependent on the overall intensity of combustion than the CO/CO_2 emission ratio. This is illustrated by (1)–(3), which suggest that the CH_4/CO ratio increases only marginally (from 8 to 11%), compared to a tenfold increase (from 2.5 to 25%) in the CO/CO_2 ratio, when CE decreases from 95 to 75%. However, larger variations in the CH_4/CO ratio have been observed from one fire to another. For example, our previously collected data, averaged by fire in Table 3, show a range of 4–12% for the CH_4/CO ratio, yet the CO/CO_2 ratios corresponding to these two extremes, for the Hardiman and Wicksted fires, respectively, differed by less than a factor of 2 (8 and 5%). Lobert et al. [1991] report a comparable range in the CH_4/CO ratio (also apparently averaged by fire) of 5–12%. Hence, it appears that the CH_4/CO ratio may be greatly influenced by fuel characteristics. This assertion is supported by the CH_4/CO ratio derived from the results of Greenberg et al. [1984], Ward et al. [1991] and Cofer et al. [1991] (Table 4), which show large differences between fuel types, with the smaller 4–6% values associated with predominantly grassy fuels (i.e., cerrado and wetlands) and larger 9–10% values with chaparral and forest-type fuels. This constitutes a relative difference of 35–45%. Smaller differences (typically <1% absolute) between CH_4/CO ratios

for the flaming and smoldering stages of combustion were reported by Cofer et al. [1991]. The CH_4/CO ratio for A121 is, rather unexpectedly, in closer agreement with the grassy fuel-type results of Greenberg et al. [1984], Ward et al. [1991], and Cofer et al. [1991] than with their results for forest-type fuels.

The CH_4/CO ratio from A121 is consistent with the previous measurements we have obtained in the plumes of 10 fires (Table 3). A mean CH_4/CO ratio of 5.5% for the first seven fires listed in Table 3 (Lodi 1 through Battersby) was initially reported by Hegg et al. [1990]. Ward and Hardy [1991] and Lobert et al. [1991] noted the relative smallness of this value. Subsequent measurements at the other three fires listed in Table 3 (Hill through Mabel Lake) yielded higher CH_4/CO ratios and raised the overall mean value of the CH_4/CO ratio to 6.7% for all ten fires.

Measurements of three gaseous nitrogen compounds were made in the smoke plume from A121 (Table 1). Several studies have shown nitrogen emissions, specifically NO_x , from biomass burning to be strongly dependent on the nitrogen content of the fuel, which typically varies from about 0.2 to 2.0% by mass for different fuels [Clements and McMahon, 1980; Susott et al., 1991; Lobert et al., 1991]. Furthermore, only a small fraction of the fuel-bound nitrogen is converted to compounds that can be measured in the field

TABLE 4. Mean Emission Ratios (Normalized to Either CO or CO_2) and Ranges for CO and Several Hydrocarbons From Various Biomass Fires

Location and Reference	Sampling Platform (Fuel Type)	Mean Emission Ratio and Range, %					
		CO/CO_2	CH_4/CO	$\text{C}_2\text{H}_6/\text{CO}$	$\text{C}_2\text{H}_2/\text{CO}_2$	$\text{C}_3\text{H}_8/\text{CO}$	$\text{C}_3\text{H}_6/\text{CO}$
Laboratory* [Lobert et al., 1991]	(Various fuels)	7.3 (3.2–16)	9.1 (5.2–12.2)	0.68 (0.16–1.05)	0.042 (0.007–0.170)	0.15 (0.02–0.32)	0.49 (0.13–0.70)
Brazil† [Greenberg et al., 1984]	Ground-based (Selva)	11.9 (4.7–30.2)	9.5	0.76		0.52	0.39
	Ground-based (Cerrado)	11.3 (4.8–26.8)	5.3	0.67		0.14	0.40
Brazil [Ward et al., 1991]	Aircraft (Selva)	8.5 (4.2–12.0)	9.7 (8.8–10.4)				
	Aircraft (Cerrado‡)	2.2	4.0				
North America†# [Cofer et al., 1991]	Helicopter (Wetlands)	5.0 (4.7–5.4)	5.9 (5.7–6.3)				
	Helicopter (Chaparral)	6.6 (5.7–8.2)	9.4 (8.1–10.6)				
	Helicopter (Boreal)	10.1 (6.7–12.1)	9.8 (9.6–10.0)				
North America* [Radke et al., 1991]	Aircraft (Various fuels)	7.9 (3.1–18.2)	6.7 (4.1–12.1)	0.52 (0.30–0.87)	0.025 (0.008–0.037)	0.16 (0.08–0.30)	0.43 (0.06–0.75)

* Data presented as overall mean values followed by range of fire-averaged mean values in parentheses.

† Originally, all data was normalized to CO_2 . $\Delta\text{X}/\Delta\text{CO}$ emission ratios were estimated by dividing the mean reported $\Delta\text{X}/\Delta\text{CO}_2$ ratio by the mean reported $\Delta\text{CO}/\Delta\text{CO}_2$ ratio.

‡ Single sample.

Ranges are from means originally reported for each burning stage (flaming, smoldering, mixed). Means are unweighted arithmetic averages of the means originally reported for each burning stage.

(it is suspected that a large quantity is converted to N_2). We do not know the average nitrogen content of the biomass consumed by A121.

The average emission factor for NO_x that we measured for A121 was $1.5 \pm 0.2 \text{ g kg}^{-1}$ (our measurements show that $\sim 85\%$ of the NO_x was in the form of NO_2). With respect to our earlier measurements in the plumes from seven fires (Table 3), this is somewhat lower than the overall average NO_x emission factor of $3.9 \pm 16 \text{ g kg}^{-1}$. However, the latter figure is strongly influenced by the measurements from two fires (Lodi 1 and Eagle) that burned in Southern California, which produced much greater quantities of NO_x . Hegg et al. [1987] suggested that this was due to the volatilization of nitrates that were originally produced in nearby Los Angeles and deposited on the vegetation prior to burning. With these two fires removed, the mean NO_x emission factor from Table 3 ($2.2 \pm 1.2 \text{ g kg}^{-1}$) is much closer to the value we measured for A121.

The NO_x/CO_2 ratio measured in the plume from A121 ranged from 0.058 to 0.105% with a mean of 0.087%. This is within the range of values found by Evans et al. [1977] (0.033–0.16%) and Andreae et al. [1988] (0.066–0.35%), which were derived from airborne measurements in fresh biomass smoke plumes in Australia and Brazil, respectively, and it is the lower limit of the range of laboratory measurements reported by Lobert et al. [1991] (0.088–0.77%). The loss of NO_x emitted from A121 by conversion to nitrates prior to sampling cannot be fully quantified, though this probably accounts for much of the variance in our measurements of the NO_x/CO_2 ratio. Figure 1 shows that the concentration of aerosol nitrate (NO_3^-) in the plume from A121 increased as the NO_x/CO_2 ratio decreased. We measured $\text{NO}_3^-/\text{NO}_x$ ratios as high as 40%; however, the total deficit of NO_x was potentially much larger due to the production of other gas phase nitrates, such as nitric acid (HNO_3) and peroxyacetyl nitrate (PAN), which were not measured.

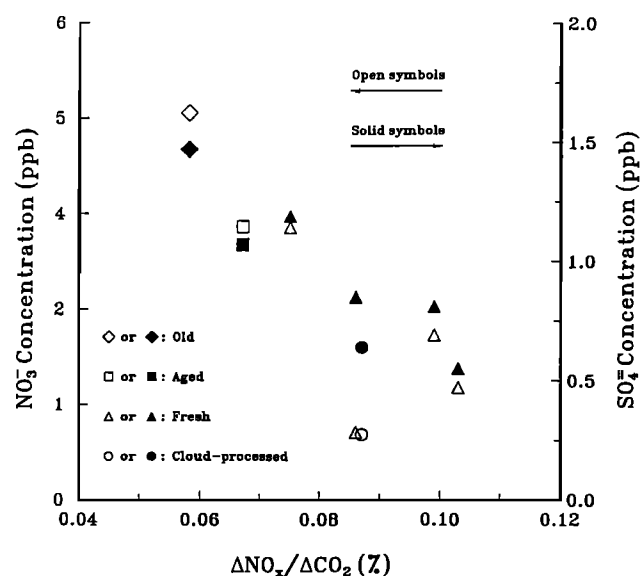


Fig. 1. Soluble nitrate and sulfate concentration versus $\Delta\text{NO}_x/\Delta\text{CO}_2$ for the smoke from the Alaska wildfire A121. ($\text{NO}_x = \text{NO} + \text{NO}_2$; on average, $\sim 85\%$ of NO_x is NO_2 .) The data points are classified by the approximate age of the sample as specified in Table 1.

The mean $\text{N}_2\text{O}/\text{CO}_2$ ratio from the data collected in Alaska was $0.009 \pm 0.005\%$. Although N_2O emissions should be well correlated with CO_2 emissions, the variance in our calculations of $\text{N}_2\text{O}/\text{CO}_2$ is understandable in view of the very small ($<1\%$) above-background enhancements that were measured for N_2O . The laboratory study of Muzio and Kramlich [1988] found significant artifact production of N_2O within canisters used to store samples of combustion gases. Subsequent experiments were performed by Cofer et al. [1990] and Winstead et al. [1991] to determine if artifact N_2O production also occurred in canisters containing diffuse samples of biomass burning emissions typical of those collected in field studies. They found significant N_2O production within the first 10 days of storage inside the canisters when the initial N_2O concentrations were relatively high. However, in most cases when the initial concentration of N_2O was less than ~ 400 ppb, there was little artifact production over a period of 3 or 4 weeks. Most of our samples showed N_2O concentrations of about 340 ppb. However, they were stored for several weeks before analysis, and the above-background enhancements measured were so slight that significant artifact production cannot be ruled out. Nevertheless, the mean $\text{N}_2\text{O}/\text{CO}_2$ ratio measured for A121 was substantially less than the range of values (0.014–0.039%) reported by Cofer et al. [1991]. Lobert et al. [1991] measured $\text{N}_2\text{O}/\text{CO}_2$ values from 0.001 to 0.028%, with a mean value of 0.009%, very much like that for A121.

The mean NH_3/CO_2 emission ratio measured in the plume from A121 was $1.3 \pm 0.5\%$. This is comparable to the 1.5% mean figure reported by Lobert et al. [1991] and the 1.8% mean figure computed from our previous measurements in the plumes of five biomass fires (Table 3). Normalization by CO_2 gives a mean NH_3/CO_2 ratio of $0.095 \pm 0.056\%$ for A121, compared to means of $0.084 \pm 0.086\%$ and $0.231 \pm 0.063\%$ measured by LeBel et al. [1991] in the smoke from prescribed fires in Florida (wetlands) and Ontario (timber-harvest debris), respectively.

Particles

The concentrations of water-soluble sulfate (SO_4^{2-}), nitrate (NO_3^-), and ammonium (NH_4^+) ions extracted from the smoke particles that were collected on Teflon filters during the afternoon and evening flights of June 28, 1990, are shown in Table 1. The highest concentrations of SO_4^{2-} and NO_3^- from A121 were found in the old smoke sampled at 2206 PDT (Table 1). This probably reflects the relatively long time available for the gas-to-particle conversion of SO_x to SO_4^{2-} and NO_x to NO_3^- . The $\text{NO}_3^-/\text{NO}_x$ ratio measured from this sample ($\sim 40\%$) was the highest of all of the samples collected (plume enhancements of SO_2 were too small to be detected above the background noise of the aircraft's SO_2 monitor), and concentrations of NO_3^- (and SO_4^{2-}) generally decreased as the NO_x/CO_2 ratio increased (Figure 1). Molar ratios of SO_4^{2-} to NO_3^- of ~ 1 were measured in samples collected at 1456 and 1513 PDT (the sample collected at 1456 PDT was processed by passage through a water cloud). Samples collected later yielded ratios of ~ 0.4 , similar to those measured in the smoke from the Lodi 1 fire in southern California (average ~ 0.3) [Hegg et al., 1987], although the concentrations of SO_4^{2-} and NO_3^- in the smoke from A121 were only about 25% of those measured in the smoke from Lodi 1.

The smoke sampled at 1456 PDT on June 28, was detained from a modest cumulus cloud that briefly capped the plume rising from A121. The concentration of NH_3 in this sample was slightly lower than the background

concentration and much lower than we measured in the fresh smoke samples, collected at 1513 and 1531 PDT, that had not passed through any water cloud. Conversely, particulate NH_4^+ was higher in the cloud-modified sample than in either of the other two samples. Molar ratios of NH_4^+ to SO_4^{2-} and NO_3^- were close to 1 in the cloud-processed smoke and 15–60% less in the two samples unaffected by cloud. This suggests that gaseous ammonia was efficiently taken up by acidic cloud droplets, and that when the cloud droplets evaporated they left behind more ammoniated, but still acidic, sulfate and nitrate-containing aerosols. The older smoke samples collected at 2041 and 2206 PDT on June 28, also had $\text{NH}_4^+/\text{SO}_4^{2-}$ and $\text{NH}_4^+/\text{NO}_3^-$ ratios less than unity. However, samples of fresh smoke collected at 2119 and 2148 PDT (emitted after the smoke samples collected at 2041 and 2206 PDT) gave higher $\text{NH}_4^+/\text{SO}_4^{2-}$ and $\text{NH}_4^+/\text{NO}_3^-$ ratios (3.1 and 1.2, respectively), suggesting that the burning conditions of the fire may have shifted in favor of ammonium production.

The mean emission factor for particles with aerodynamic diameters $<3.5\ \mu\text{m}$ ($\text{PM}_{3.5}$) was $21.3 \pm 4.3\ \text{g kg}^{-1}$. Ward and Hardy [1991] derived an empirical relation between the $\text{PM}_{2.5}$ emission factor [$\text{EF}(\text{PM}_{2.5})$] and CE, based on data for different fuel types (primarily timber-harvest debris and standing chaparral) in Washington, Oregon, and California, where particulate matter and gaseous samples were collected within about 10 m of the ground:

$$\text{EF}(\text{PM}_{2.5}) = 67.4 - 66.8\ \text{CE} \quad (r = -0.86) \quad (4)$$

where, $0 \leq \text{CE} \leq 1$, r is the correlation coefficient, and the units for $\text{EF}(\text{PM}_{2.5})$ are g kg^{-1} . Substituting the mean CE computed for A121 (0.895) into (4) gives an emission factor of $7.6\ \text{g kg}^{-1}$. This is a factor of about 3 smaller than that measured for A121. (Size spectra of smoke particles suggest those particles between 2.5- and $3.5\text{-}\mu\text{m}$ diameter contribute very little to $\text{PM}_{3.5}$.) We checked our particle mass concentration measurements against concurrent measurements of the optical scattering coefficient due to particles (b_{sp}). The results are plotted in Figure 2 with a regression line constrained through the origin. The inverse of the slope of the regression line ($4.1 \pm 0.1\ \text{m}^2\ \text{g}^{-1}$) is an estimate of the specific scattering coefficient (B_s) of the smoke particles ($B_s = \sigma_{\text{sp}}/\rho$ where ρ is the mass concentration of particles determined from the Teflon filter samples). Tangren [1982] recommends a value of $5\ \text{m}^2\ \text{g}^{-1}$ for airborne measurements of B_s in biomass smoke. Measurements of unaged smoke sampled in the laboratory [Patterson and McMahon, 1984] and from the ground near field fires [Tangren, 1982] give B_s values of $\sim 3.5\ \text{m}^2\ \text{g}^{-1}$. This suggests that our measurements of particle mass concentration are probably accurate to within about +20%. Since an error of about +200% is required to explain the disagreement between (4) and the fine-particle emission factor for A121, it would seem that the old boreal forest fuels consumed by A121 are capable of producing substantially more particulate mass when burned than the chaparral and timber-harvest debris studied by Ward and Hardy [1991]. However, (4) generally underestimates the fine-particle emission factors listed in Table 3 (i.e., fire-averaged emission factors computed from data we have collected previously during studies of other fires). For example, the overall mean $\text{PM}_{3.5}$ emission factor from Table 3 is $14.4 \pm 10.1\ \text{g kg}^{-1}$, corresponding to an overall mean CE of 90%. Equation (4), on the other hand, predicts a $\text{PM}_{2.5}$ emission factor of only $7.3\ \text{g kg}^{-1}$. Hence, attribution of the

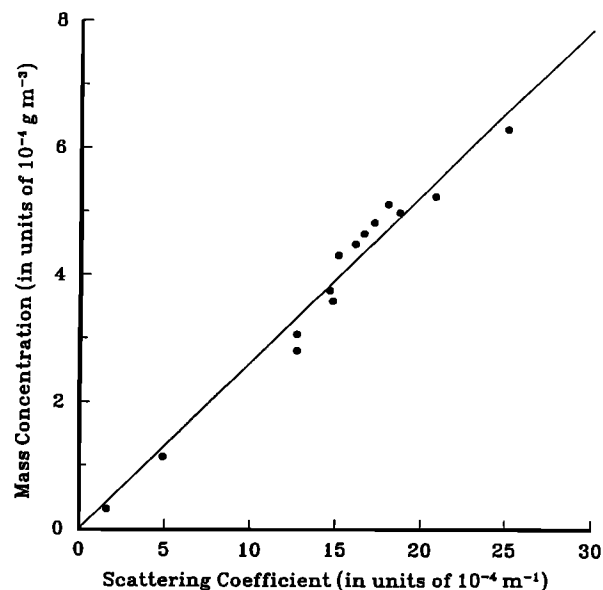


Fig. 2. Mass concentration of particles versus the coefficient of light scattering due to particles (at $\lambda = 540\ \text{nm}$) for the Alaska wildfire A121. A least squares fit through the origin is represented by the solid line with a slope of $0.25\ \text{g m}^{-2}$.

disagreement between the mean fine-particle emission factor measured for A121 and that predicted by (4) to simple differences in fuel/ecosystem types would be hasty. Ground-based and airborne measurements of smoke particles from the same fires are needed to determine if these two independent methods give similar results.

Conclusions

In this paper, we have described measurements of gaseous and particulate emissions from a wildfire (A121) that burned in an old black spruce forest in Alaska during the summer of 1990. The relative proportions of the various carbon compounds emitted, expressed as molar ratios and emission factors, are generally consistent with the results of other laboratory and field studies of biomass burning. Possible exceptions are (1) the mean fine-particle emission factor, which was about 3 times larger than that predicted by a regression relation derived by Ward and Hardy [1991], which has combustion efficiency as the independent variable, and (2) the mean CH_4/CO molar emission ratio, which was at the low end of a range of values measured by other investigators [Greenberg et al., 1984; Lobert et al., 1991; Cofer et al., 1991; Ward and Hardy, 1991]. The emission factor for particles $<3.5\ \mu\text{m}$ diameter and the CH_4/CO emission ratio measured in the smoke from the Alaskan wildfire were consistent with the overall mean values derived from our previous airborne measurements in smokes from several other prescribed fires and wildfires.

Our measurements of nitrogen compounds emitted from the Alaskan wildfire are generally consistent with the results of other studies but comparatively low relative to our airborne measurements in smokes from other fires. The measurements of NH_3/CO and $\text{N}_2\text{O}/\text{CO}_2$ emission ratios are very close to the overall mean values reported in the laboratory study of Lobert et al. [1991]. The NO_x/CO_2 emission ratio that we measured for the Alaskan wildfire is

somewhat lower than that measured by Lobert et al. [1991]. However, our NO_x/CO_2 ratio does not take into account the conversion of NO_x to nitrates in the atmosphere. Molar ratios of water-soluble, aerosol nitrate to NO_x in the smoke from the Alaskan wildfire ranged from ~5 to ~40%.

Measurements of gaseous NH_3 and particulate NH_4^+ , NO_3^- , and SO_4^{2-} , obtained in the smoke just downwind of a water cloud that briefly formed over the Alaskan wildfire, indicate that NH_3 was efficiently taken up by cloud droplets, where it helped to partially neutralize the sulfate and nitrate content of the aerosols left behind after evaporation of the cloud droplets.

Acknowledgments. We are especially appreciative of the Alaska Fire Service for hosting and supporting our air operations in Alaska. We also thank all members of the University of Washington aircraft crew for their considerable contributions to this project. We thank R. A. Rasmussen for analyzing the canister samples, and R. J. Ferek for analyzing the ionic content of the smoke particles. This research was supported by funds provided by the Defense Nuclear Agency under project IACRO 89-903, Task RA, work unit 00024; and Intermountain Research Station, Forest Service, U.S. Department of Agriculture. The government has certain rights to this material but does not necessarily endorse its contents.

References

- Andreae, M. O., E. V. Browell, M. Garstang, G. L. Gregory, R. C. Harriss, G. F. Hill, D. J. Jacob, M. C. Pereira, G. W. Sachse, A. W. Setzer, P. L. Silva Dias, R. W. Talbot, A. L. Torres, and S. C. Wofsy, Biomass-burning emissions and associated haze layers over Amazonia, *J. Geophys. Res.*, **93**, 1509–1527, 1988.
- Bollen, W. B., Soil microbes, in Environmental Effects of Forest Residues Management in the Pacific Northwest, A State-of-Knowledge Compendium, *Gen. Tech. Rep. PNW-24*, pp. B1–B4, USDA For. Serv., Pac. Northwest For. and Range Exp. St., 1974.
- Bryam, G. M., Combustion of forest fuels, in *Forest Fire Control and Use*, edited by K. P. Davis, McGraw-Hill, New York, 1959.
- Clements, H. B., and C. K. McMahon, Nitrogen oxides from burning forest fuels examined by thermogravimetry and evolved gas analysis, *Thermochim. Acta*, **35**, 133–139, 1980.
- Cofer, W. R., III, J. S. Levine, E. L. Winstead, and B. J. Stocks, Gaseous emissions from Canadian boreal forest fires, *Atmos. Environ.*, **24A**, 1653–1659, 1990.
- Cofer, W. R., III, J. S. Levine, E. L. Winstead, and B. J. Stocks, Trace gas and particulate emissions from biomass burning in temperate ecosystems, in *Global Biomass Burning: Atmospheric, Climatic, and Biospheric Implications*, edited by J. S. Levine, pp. 203–208, MIT Press, Cambridge, Mass., 1991.
- Dasch, J. M., Particulate and gaseous emissions from wood-burning fireplaces, *Environ. Sci. Tech.*, **16**, 639–645, 1982.
- Evans, L. F., I. A. Weeks, A. J. Eccleston, and D. R. Packham, Photochemical ozone in smoke from prescribed burning of forests, *Environ. Sci. Tech.*, **11**, 896–900, 1977.
- Greenberg, J. P., P. R. Zimmerman, L. Heidt, and W. Pollock, Hydrocarbon and carbon monoxide emissions from biomass burning in Brazil, *J. Geophys. Res.*, **89**, 1350–1354, 1984.
- Hegg, D. A., L. F. Radke, P. V. Hobbs, C. A. Brock, and P. J. Riggan, Nitrogen and sulphur emissions from the burning of forest products near large urban areas, *J. Geophys. Res.*, **92**, 14,701–14,709, 1987.
- Hegg, D. A., L. F. Radke, P. V. Hobbs, R. A. Rasmussen, and P. J. Riggan, Emissions of some trace gases from biomass fires, *J. Geophys. Res.*, **95**, 5669–5675, 1990.
- Hobbs, P. V., L. F. Radke, J. H. Lyons, R. J. Ferek, D. J. Coffman, and T. J. Casadevall, Airborne measurements of particle and gas emissions from the 1990 volcanic eruptions of Mount Redoubt, *J. Geophys. Res.*, **96**, 18,735–18,752, 1991.
- LeBel, P. J., S. A. Vay, and P. D. Roberts, Ammonia and nitric acid emissions from wetlands and boreal forest fires, in *Global Biomass Burning: Atmospheric, Climatic, and Biospheric Implications*, edited by J. S. Levine, pp. 225–229, MIT Press, Cambridge, Mass., 1991.
- Lobert, J. M., D. H. Scharffe, W. Hao, T. A. Kuhlbusch, R. Seuwen, P. Warneck, and P. J. Crutzen, Experimental evaluation of biomass burning emissions: nitrogen and carbon containing compounds, in *Global Biomass Burning: Atmospheric, Climatic, and Biospheric Implications*, edited by J. S. Levine, pp. 289–304, MIT Press, Cambridge, Mass., 1991.
- Muzio, L. J., and J. C. Kramlich, An artifact in the measurement of N_2O from combustion sources, *Geophys. Res. Lett.*, **15**, 1369–1372, 1988.
- Patterson, E. M., and C. K. McMahon, Absorption characteristics of forest fire particulate matter, *Atmos. Environ.*, **18**, 2541–2551, 1984.
- Radke, L. F., D. A. Hegg, J. H. Lyons, C. A. Brock, P. V. Hobbs, R. E. Weiss, and R. A. Rasmussen, Airborne measurements on smokes from biomass burning, in *Aerosols and Climate*, edited by P. V. Hobbs and M. P. McCormick, pp. 411–422, A. Deepak, Hampton, Va., 1988.
- Radke, L. F., D. A. Hegg, P. V. Hobbs, J. D. Nance, J. H. Lyons, K. K. Laursen, R. E. Weiss, P. J. Riggan, and D. E. Ward, Particulate and trace gas emissions from large biomass fires in North America, in *Global Biomass Burning: Atmospheric, Climatic, and Biospheric Implications*, edited by J. S. Levine, pp. 209–224, MIT Press, Cambridge, Mass., 1991.
- Rasmussen, R. A., and M. A. K. Khalil, Atmospheric halocarbons: Measurements and analyses of selected trace gases, *Proceedings of the NATO Advanced Study Institute on Atmospheric Ozone*, edited by A. C. Aikin, U.S. Dep. Transport., Washington, D.C., 1980.
- Rasmussen, R. A., and M. A. K. Khalil, Atmospheric methane (CH_4): Trends and seasonal cycles, *J. Geophys. Res.*, **86**, 9826–9832, 1981.
- Rasmussen, R. A., H. H. Westberg, and M. Holdren, Need for standard referee GC methods in atmospheric hydrocarbon analysis, *J. Chrom. Sci.*, **12**, 80–85, 1974.
- Susott, R. A., D. A. Ward, R. E. Babbit, and D. J. Latham, The measurements of trace emissions and combustion characteristics for a mass-fire, in *Global Biomass Burning: Atmospheric, Climatic, and Biospheric Implications*, edited by J. S. Levine, pp. 245–257, MIT Press, Cambridge, Mass., 1991.
- Tangren, C. D., Scattering coefficient and particulate matter concentration in forest fire smoke, *J. Air Poll. Control Assoc.*, **32**, 729–732, 1982.

- Ward, D. E., D. V. Sandberg, R. D. Ottmar, J. A. Anderson, G. C. Hofer, and C. K. Fitzsimmons, Measurements of smokes from two prescribed fires in the Pacific Northwest, in Proceedings of Seventy-fifth Annual Meeting of the Air Pollution Control Association, (Available from D. E. Ward, USDA Forest Service, Intermountain Fire Science Laboratory, Missoula, MT 59807), 1982.
- Ward, D. E., and C. C. Hardy, Organic and elemental profiles for smoke from prescribed fires, in Receptor Models in Air Resource Management: Proceedings of International Specialty Conference, edited by J. G. Watson, pp. 299–321, Air and Waste Manag. Assoc., Pittsburgh, Pa., 1988.
- Ward, D. E., and C. C. Hardy, Smoke emissions from wildland fires, Environ. Int., **17**, 117–134, 1991.
- Ward, D. E., A. W. Setzer, Y. J. Kaufman, and R. A. Rasmussen, Characteristics of smoke emissions from biomass fires of the Amazon Region – BASE-A Experiment, in Global Biomass Burning: Atmospheric, Climatic, and Biospheric Implications, edited by J. S. Levine, pp. 394–402, MIT Press, Cambridge, Mass., 1991.
- Winstead, E. L., W. R. Cofer, and J. S. Levine, Emissions of nitrous oxide from biomass burning, in Global Biomass Burning: Atmospheric, Climatic, and Biospheric Implications, edited by J. S. Levine, pp. 376–378, MIT Press, Cambridge, Mass., 1991.
- J. D. Nance, and P. V. Hobbs, Department of Atmospheric Sciences, AK-40, University of Washington, Seattle, WA 98195.
- L. F. Radke, Research Aviation Facility, National Center for Atmospheric Research, PO Box 3000, Boulder, CO 80307-3000.
- D. E. Ward, Intermountain Fire Science Laboratory, USDA Forest Service, PO Box 8089, Missoula, MT 59807.

(Received September 8, 1992;
revised April 19, 1993;
accepted April 29, 1993.)